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THE MELTING BEHAVIOR OF TNT (U)

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THE MELTING BEHAVIOR OF TNT

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ABSTRACT: Results of a dilatometric study of TNT have shown that considerable amounts of liquid TNT can exist at temperatures below the melting point. At 75°C, two samples of Grade I TNT showed 5.2% and 7.4% liquid TNT. A purified sample of TNT showed no liquid at the same temperature.

Over the range of 50° to 64°C the linear and cubical expansion of TNT was found to be 1.01×10^{-4}/°C and 3.03×10^{-4}/°C, respectively.

A discontinuity in the data was observed between 64° and 65°C, which was ascribed to a solid-solid phase transition.

A theoretical discussion is given of the predicted melting behavior of TNT.

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This report describes the melting of TNT under conditions of elevated temperature storage but considerably below the recognized melting point. The information should be helpful in establishing quality standards as well as maximum allowable storage temperatures for TNT loaded weapons.

This work was performed under Task No. 301-664/43006/08.

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By direction

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INTRODUCTION

For several years there has been concern over the formation of liquid TNT during long-term storage of TNT loaded weapons. Following World War I, liquid TNT often was observed exuding from stored warheads. Such liquid resulted from low melting eutectics of the alpha TNT with impurities consisting of largely beta and gamma TNT, as well as 2,4-dinitrotoluene. The amount of liquid exudate was a function of several variables including nature of the impurities, their amounts and the storage conditions.

Improvements in manufacturing and purification developed prior to World War II have led to a military grade of TNT of higher quality, designated as Grade I. In spite of the improved quality, there have been reports of TNT exudation from shells (1) and mines (2).

Exudation may produce a cavity in the loaded weapon, which is perhaps the major objection to it. If the cavity is under the booster, the charge may fail to detonate. Grain growth and lack of dimensional stability are more subtle undesirable changes resulting from liquid formation in TNT castings.

Questions have arisen from time to time as to the probability of exudate formation in TNT or TNT based munitions under conditions of elevated temperature storage. In order to better answer these questions, a study has been made of the melting behavior of TNT.

As there is a relatively large volume change during the solid to liquid transition, a dilatometric method was used to study progressive volume changes occurring in the sample as a function of temperature. The dilatometric technique was found to be satisfactory, as reported herein.

RESULTS AND DISCUSSION

Data in the form of curves are given in Figures 1, 2, 3 and 4 in which capillary height in the dilatometer is plotted as a function of temperature. Changes in the capillary height are produced by the cumulative effects of water, sample and glass expansion. At the lower end of the curve it is assumed that no liquid TNT is present in the dilatometer.

The amount of liquid TNT calculated to be present in each of the four samples in the dilatometers as a function of temperature is given in Table I below. In order to calculate the values in this table it is necessary to estimate the position on the curve where the slope is beginning to increase. Liquid in the Composition B sample had to be determined graphically owing to absence of data on the thermal expansion of solid RDX.

TABLE I

PERCENT LIQUID IN TNT

Temperature, °C	Sample: Granular Production	Flake Production	Granular Purified	Comp. B Production
70.0	0.35	0.46	nil	0.2
73.9 (165°F)	2.9	4.2	nil	2.7
75.0	5.2	7.4	nil	16.8

The percentages of liquid shown in Table I do not include some additional liquid known to exist in production grade TNT at temperatures far below those shown. Exudation has been observed in TNT and Composition B loaded shells stored at 65°C for five months (3). Certainly a small amount of liquid exists in a TNT casting above 44.4°C, the ternary $\alpha\beta\gamma$ TNT eutectic melting point (4). Infrared spectrophotometric analyses of TNT exudate (1), collected from several 90 mm shells loaded with Grade I TNT stored only four days at 71°C, showed that the exudate consisted chiefly of α TNT with the following average percentages of impurities: β TNT, 3.1%; γ TNT, 6.1% and 2,4-dinitrotoluene, 5.1%. The ratio of the γ to the β isomer is close to that found in the $\alpha\beta\gamma$ TNT ternary eutectic composition.

Table II below shows the amount of liquid TNT calculated to be present in a cast charge at several temperatures at two levels of impurity, 0.5% and 1.0%. It is assumed that the impurity consists of β and γ TNT in the same ratio as present in the ternary eutectic composition (4). Finnie and Rowson (5) have determined the purity of one sample of service grade TNT of U. S. origin and found it to be 99.4% pure. Thus, the values shown in Table II are believed to be a realistic level of liquid possible in a cast charge.

TABLE II

PERCENT LIQUID TNT IN A CAST
CHARGE CONTAINING BETA AND GAMMA TNT

Temperature, °C	Total β and γ TNT	
	0.5%	1.0%
44.4	0.88	1.77
60.0	1.43	2.86
65.0	1.82	3.64
70.0	2.72	5.44

The granular purified TNT, Table I, showed no liquid formation at 75°C based on the dilatometric measurements. Although the sample must contain some small amount of impurity, it could not be detected by the method used. The difference between the purified sample and the two production samples, Table I, shows clearly the effect of purity on liquid formation in the range of 70° to 75°C.

No precise maximum allowable temperature can be given for the storage of TNT loaded weapons, because the amount of liquid that will form in a cast charge is also a function of other variables such as the type and quantity of impurities present. However, the results reported herein, as well as the work of other investigators suggest that 65°C is close to the maximum storage temperature for production quality TNT if significant quantities of liquid are to be avoided.

Over the range of temperatures where no melting was detected, our measurements allow a calculation of the coefficient linear and cubical expansion of TNT, Table III. The values for the linear coefficient of expansion represent the average expansion along the three crystallographic directions. Eubank and Van Dolah (6) have measured the coefficient of linear expansion along each of the three crystallographic axes. They did not report a value for the cubical expansion of TNT, but this can be calculated readily. The calculated value, 2.78×10^{-4} per °C, is in reasonably good agreement with our data. The Naval Ordnance Test Station measurements covered a temperature range of about 25 to 75°.

TABLE III

COEFFICIENT OF THERMAL EXPANSION OF TNT

	NOL	NOTS
Average Linear (50 - 64°C)	1.00×10^{-4}/°C 1.02×10^{-4}	*
Cubical (50 - 64°C)	3.01×10^{-4}/°C 3.05×10^{-4}	2.78×10^{-4} **

* Reported for the three crystallographic axes
** Calculated value

Several literature values of the linear expansion of TNT are given in a report prepared by the Armour Research Foundation (7). There is gross disagreement among the values. The very high values may result from the solubility of air in TNT (8), or inclusions of trapped gas within a large charge.

Results have been reported on the density of TNT at 25°C prepared from an air-free melt. Small air-free TNT castings at 25°C have an average density of 1.630 (8). The difference between 1.630 and the crystal density, 1.654, represents the voids produced as a result of shrinkage of the solid TNT as it cools. It is not possible, except under the most ideal conditions, to obtain a TNT density at 25°C greater than 1.637 by a casting technique. This calculated value, 1.637, is based on a crystal density of 1.654, a coefficient of cubical expansion of 3.03×10^{-4} per °C and the absence of appreciable supercooling during crystallization.

We observed a discontinuity in our dilatometric measurements between 64 and 65°C. It is believed that the observed inflection results from a solid-solid polymorphic transition. Similarly, Eubank and Van Dolah (6) observed an inflection in their expansion curves near 64°C and ascribed this to a polymorphic transition. They attempted to confirm this transition by accurate calorimetric measurements but were unsuccessful. At least three crystalline modifications of TNT have been reported (9), although the stability ranges and the interrelationship of the three forms are not known.

THEORETICAL CONSIDERATIONS

The thermodynamic prediction of the behavior of Grade I TNT is considerably simplified because the impurities present are almost entirely the isomers 2,3,4-trinitrotoluene, beta TNT; 2,4,5-trinitrotoluene, gamma TNT; and 2,4-dinitrotoluene, (1), typically present in about the ratio 1:2:2. These substances are so similar to TNT that only small error seems possible in considering their mutual solutions with each other and with TNT to be ideal. For this to be true over large concentration ranges, the escaping tendency of a molecule of alpha or ordinary TNT must be the same when it is surrounded by say, beta TNT, as when it is surrounded in the liquid by its own kind of molecules. This is a rigorous requirement, as it has as a consequence (10) that no volume change occurs on mixing the liquid, or fused components, that they are miscible in all proportions, that there is no heat of mixing of the liquid or fused components, and that if one or more of the components are solids, the heat of mixing to form the solution is just the absorption of enough heat to melt the solids. Thus, partially miscible liquids or those evolving heat on mixing cannot possibly form ideal solutions.

Two-Component Ideal Solutions

Considerable insight into the phenomena involved in fusion phenomena can be acquired through examination of the simplest possible condensed phase solution, a two-component ideal solution in which the liquids are miscible but the solids mutually insoluble. The relations are particularly simple when concentrations are expressed in mole fractions,

$$N_A = \frac{\text{number of moles of A}}{\text{number of moles of A + number of moles of B}}, \text{ etc.}$$

In our case, $N_A + N_B = 1$; in three component systems $N_A + N_B + N_C = 1$, etc.

In a saturated ideal solution of solid A in liquid B, the escaping tendency of A in the liquid and the solid must be the same. This has as a consequence (10)

$$d\ln N_A = \frac{\Delta H_A}{RT^2} dT, \qquad (1)$$

where N_A is the mole fraction of the solid A in the solution, ΔH_A is the heat absorbed on melting one mole of A at its melting point T_A, R is the gas constant and T is the absolute temperature. Since when $N_A = 1$, the solution is pure A and and melts at T_A, we can integrate equation (1) between the limits $N_A = 1$, $T = T_A$ and $N_A = N_A$, $T = T$. This results in the remarkable relation $-\ln N_A = \frac{\Delta H_A}{R} \frac{T_A - T}{T_A T}$, or, inserting the value of R in calories per degree and changing to common logarithms,

$$- \log N_A = (\Delta H_A/4.575)\ (T_A - T)/T_A T \qquad (2)$$

The remarkable feature of equation (2) is that it contains only the properties of A. The solubility of A at a given temperature depends only on the heat of fusion of A and is the same in all solvents so long as the solution is ideal. Note that the solubility is greater at higher temperatures.

One important application of equation (2) can be made at once. At the melting point, the temperature at which the last crystal of TNT has just disappeared in the melt, the solution is saturated with TNT, as it is in equilibrium with the solid. If this melting point is lower than that for pure TNT, 80.90°C (5) or 354.06°A, not only is it known that the TNT is not pure, but the mole fraction of the impurity has been measured, and, with one further fact discussed below, the proportion of liquid is known at all temperatures.

So far the heat of fusion has been supposed to be independent of the temperature. It can be readily shown (10) that $d\Delta H/dT = \Delta C_p$, where ΔC_p is the difference of the heat capacity at constant pressure of the liquid and the solid. Since the liquid melt has a larger heat capacity than the solid, ΔC_p is positive, and the heat of fusion decreases as the temperature is lowered. This correction is generally small, as ΔC_p is usually near 13 calories per mole per degree, but is rather 8.63 calories per mole for TNT. When it must be used, as when the temperature is more than a few degrees below the melting point, equation (2) becomes

$$-\log N_A = \frac{\Delta H_A}{4.575\ T_A} \frac{T_A - T}{T} - \frac{\Delta C_p}{4.575} \frac{T_A - T}{T} - \frac{\Delta C_p}{1.987} \log \frac{T_A}{T} \qquad (3)$$

Eutectics

The other constituent, or constituents in a multicomponent solution, behaves in exactly the same way. The solution can be regarded as a solution of B in A just as well as A in B. If the heat of fusion, ΔC_p and melting temperature of B is used in equation (3), the result is the solubility of B as a function of temperature. If a two-component solution is cooled, a temperature will be reached at which one constituent, B or A, will crystallize out, depending on the proportions of A and B in the original mixture. This process cannot continue indefinitely, as if B crystallizes out, on further cooling the liquid portion becomes more and more concentrated in A, until it finally becomes saturated. The liquid thus is saturated with both components, and they crystallize out together. The temperature and composition at which this occurs is the eutectic temperature and composition. In an ideal solution, no liquid phase can exist below the eutectic temperature. At the eutectic temperature all of one or the other component melts with enough of the other to make a liquid of the eutectic composition. Further rise in temperature causes solution of the component present in greater proportion than in the eutectic, until, at some temperature below its melting point, it is all dissolved in the liquid.

Thus, in a casting of impure TNT, no liquid forms until the temperature is attained, at which the eutectic formed by the impurities with the TNT melts. This eutectic temperature is the one further fact needed to define the melting behavior completely. Figure 5 illustrates this behavior for impurities producing a eutectic melting at 46°C, about that found in Grade I TNT. Figure 5 is the ideal solubility of TNT as a function of temperature, plotted from the data of Table IV, calculated using 5,075 calories per mole for the heat of fusion of TNT (5) and ΔC_p = 8.63 calories per mole (11).

TABLE IV

THE IDEAL SOLUBILITY OF TNT

T, °C	Mole Fraction
80.90	100.00
80.70	99.54
80.30	98.65
80.00	97.97
79.70	97.31
79.30	96.42
79.00	95.74
78.00	94.22
75.00	88.34
72.00	82.40
68.00	76.36
64.00	70.03
60.00	64.11
55.00	57.32
50.00	51.11
45.00	45.45
40.00	40.13
35.00	35.67

EXPERIMENTAL

Dilatometers

The dilatometers were constructed as shown in Figure 6 using a sample tube of about 3 cc capacity. Capillaries were tested for uniformity of bore and their volumes per unit length were determined by calibration with mercury. Reference marks were sandblasted on the 1 mm capillary tubing used for the dilatometers. After the volume of the dilatometer had been measured, an accurately weighed sample of about 2.5 g of explosive was added to the sample tube. The 12/18 standard tapered joint was sealed with a thin film of Scotchcast Resin No. 2 and allowed to cure for at least twenty-four hours. Distilled water was added to the dilatometer by means of a three-way stopcock after evacuation for about an hour with a Megavac pump. A Burgess "vibro-tool" proved helpful in loosening the sample particles for easy removal of trapped air. After adjusting the height of the water, the capillary was sealed. Overall length of the dilatometer was about fourteen inches.

Procedure

The dilatometers were held rigidly in a metal rack and completely immersed in a constant temperature bath held to within 0.02°C. No readings were taken at the starting temperature (about 50°C) until the dilatometers had been immersed for 48 hours to insure solubility equilibrium. The liquid level was measured with a Gaertner 100 mm micrometer slide cathetometer. Further readings were taken at 2 to 3°C intervals until about 65°C. Above 65°C the temperature interval was reduced to about 1°C or less.

Samples

Purified TNT. This sample was obtained from R. W. Van Dolah of the Naval Ordnance Test Station, China Lake, California. No data was supplied with respect to the mole percent impurity estimated in the sample.

Granular TNT, Grade I, manufacturer unknown.

Flake TNT, Grade I, Keystone Ordnance Works.

Comp B, Production Grade, Holston Ordnance Works.

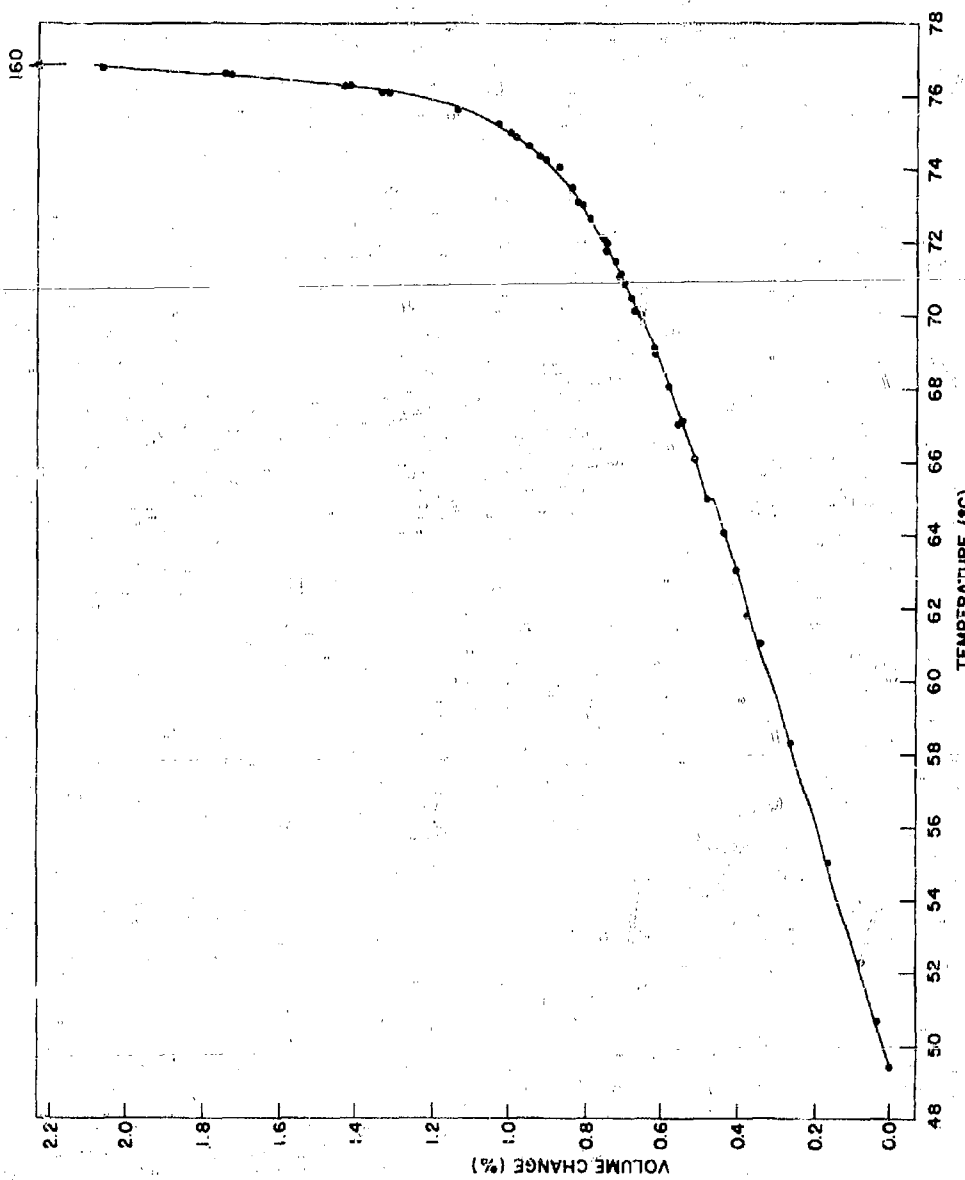

FIG.1 VOLUME CHANGE OF GRANULAR TNT (X-159)

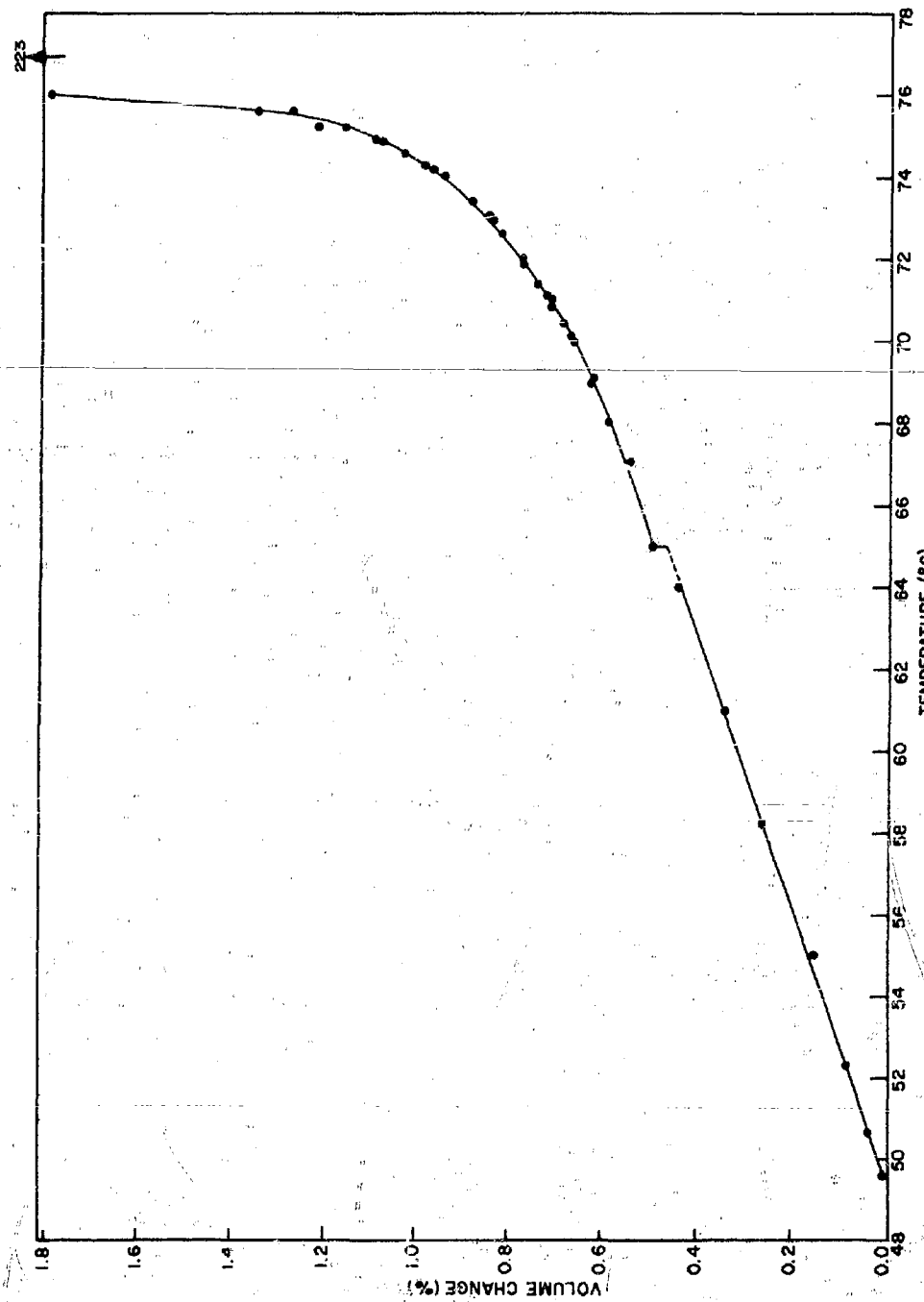

FIG.2 VOLUME CHANGE OF FLAKE TNT (X-203)

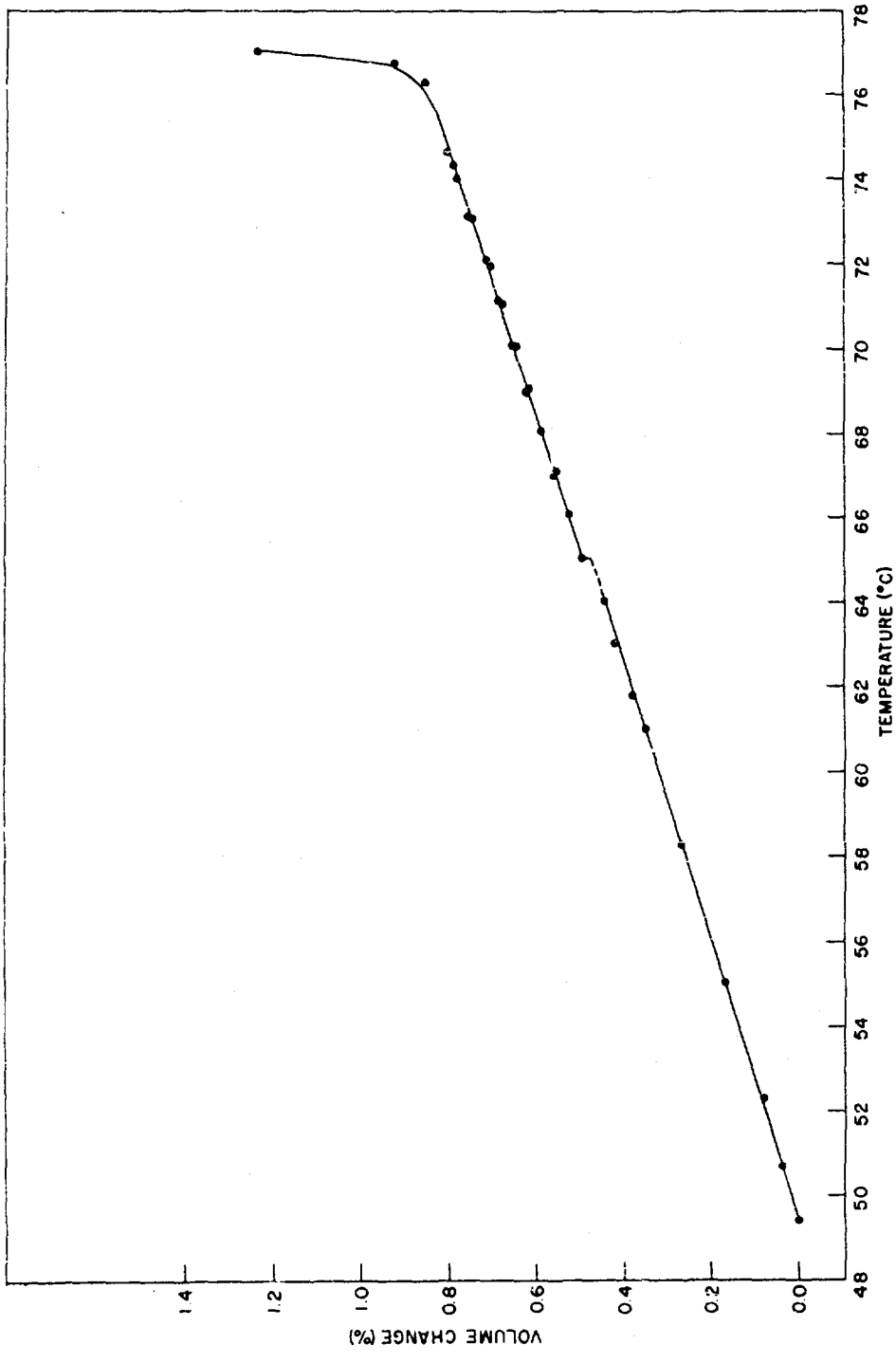

FIG.3 VOLUME CHANGE OF GRANULAR TNT (PURIFIED SAMPLE)

TEMPERATURE (°C)

FIG.3 VOLUME CHANGE OF GRANULAR TNT (PURIFIED SAMPLE)

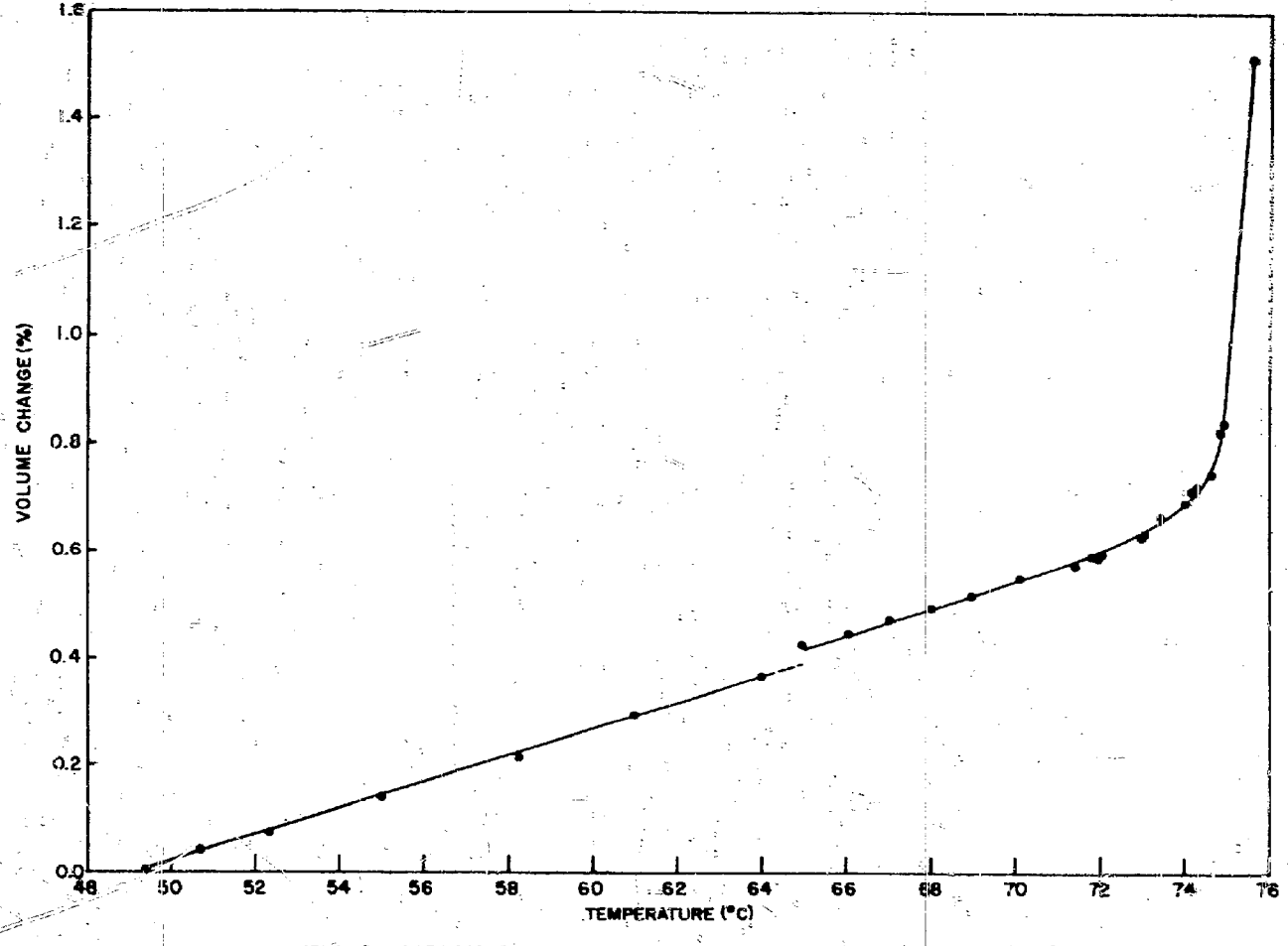

FIG.4 VOLUME CHANGE OF COMPOSITION B (X-261)

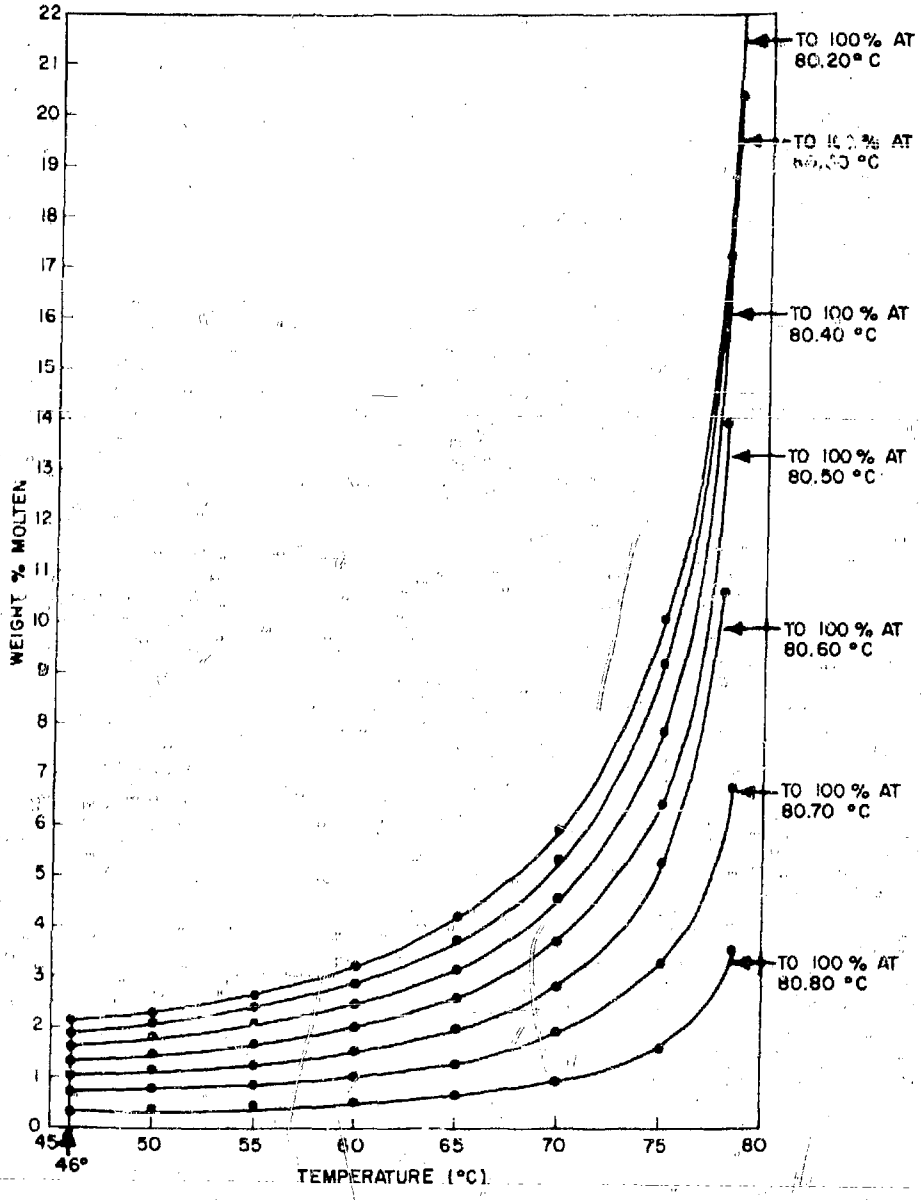

FIG. 5 WEIGHT PERCENT LIQUID AS A FUNCTION OF TEMPERATURE FOR IMPURE TNT

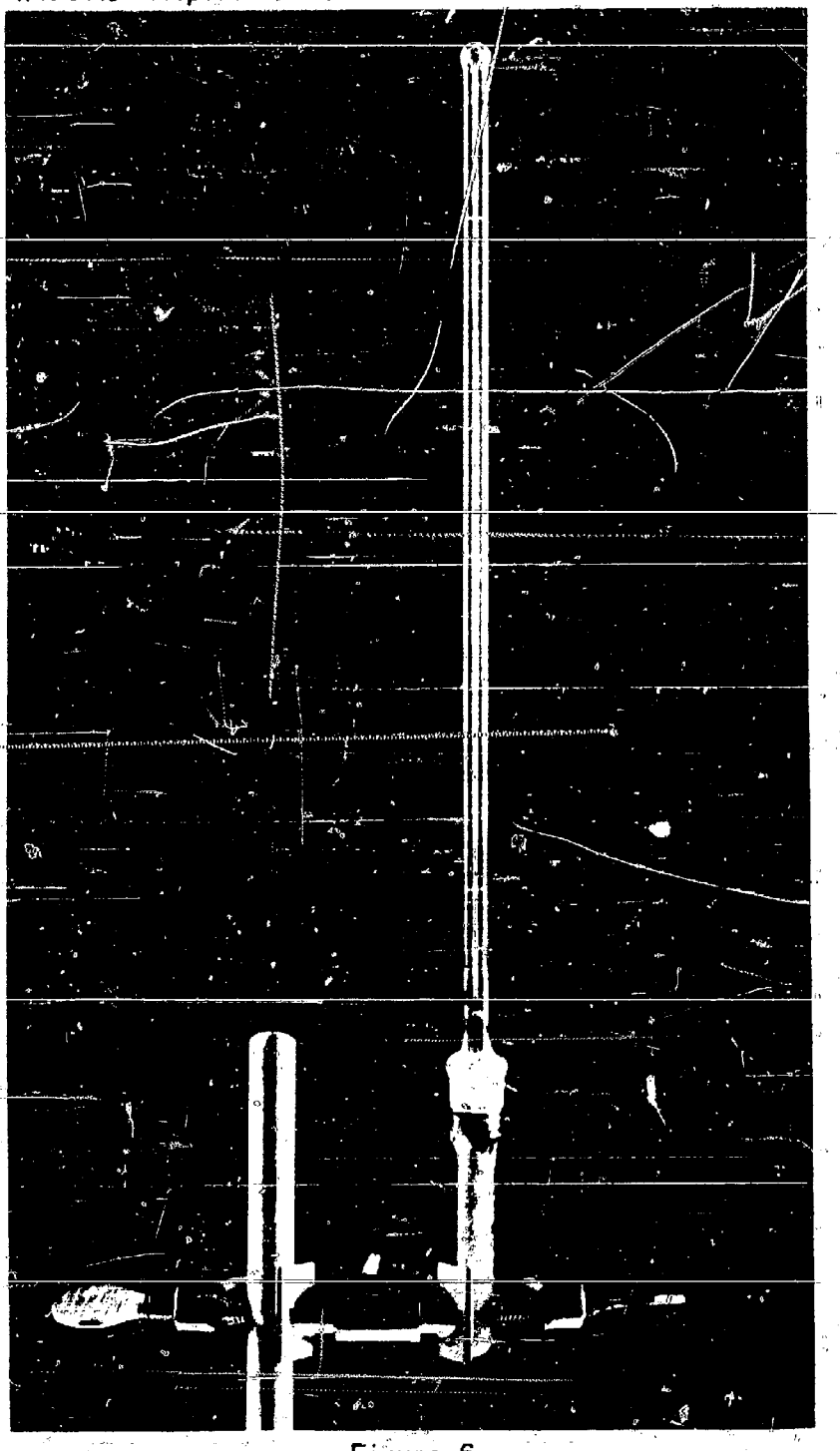

Figure 6
DILATOMETER

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